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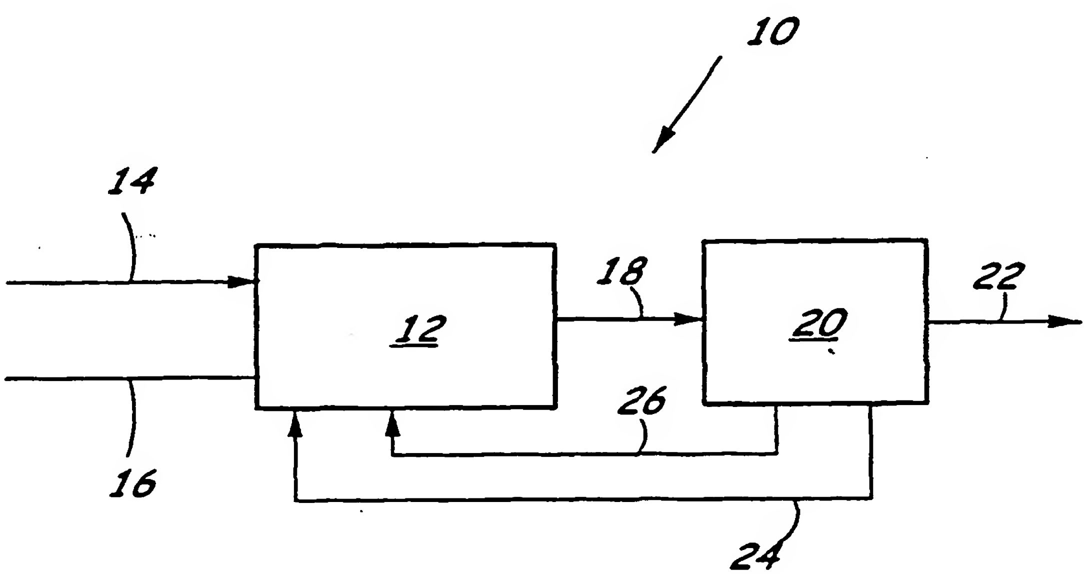
[Continued on next page]

(54) Title: PRODUCTION OF OXYGENATED PRODUCTS



(57) Abstract: A process for producing oxygenated products from an olefinic feedstock, which process includes reacting, in a hydroformylation reaction stage, an olefin feedstock with carbon monoxide and hydrogen at elevated temperature and superatmospheric pressure in the presence of a hydroformylation catalyst. The hydroformylation catalyst comprises a mixture of a metal, M, where M is cobalt (Co), rhodium (Rh), ruthenium (Ru) or palladium (Pd); carbon monoxide; and a bicyclic tertiary phosphine having a ligating phosphorus atom. The ligating phosphorus atom is neither in a bridgehead position nor a member of a bridge linkage. The process produces oxygenated products comprising aldehydes and/or alcohols.

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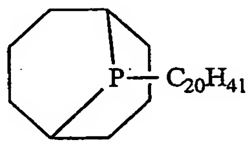
PRODUCTION OF OXYGENATED PRODUCTS

THIS INVENTION relates to the production of oxygenated products. It relates in particular to a process for producing oxygenated products from an olefinic feedstock, and to a hydroformylation catalyst.

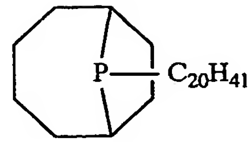
Hydroformylation processes for the production of oxygenated products, particularly aldehydes and/or alcohols, by the reaction of an olefinic feedstock with carbon monoxide and hydrogen at elevated temperatures and pressures in the presence of hydroformylation catalysts, are well known. The alcohols and/or aldehydes that are produced in these processes generally correspond to the compounds obtained, in the hydroformylation reaction, by the addition of a carbonyl or carbinol group to an olefinically unsaturated carbon atom in the feedstock with simultaneous saturation of the olefin bond.

A hydroformylation catalyst is selected according to the particular oxygenated products which are required from a particular olefinic feedstock. Thus, the hydroformylation catalyst may typically be a phosphine and/or phosphite ligand modified rhodium (Rh) or cobalt (Co) homogeneous catalyst. Examples of such catalysts are triphenyl phosphine ligands used with rhodium, and alkyl phosphine ligands used with cobalt. Specific examples of the latter are trialkyl phosphines and bicyclic tertiary phosphines such as 9-phosphabicyclo [3.3.1] nonane and

9-phosphabicyclo [4.2.1] nonane represented by formulas (I) and (II) respectively:



I



II

The ligands **I** and **II** are available commercially, as a mixture, under the collective chemical name eicosyl phoban ('EP').

A disadvantage of Co catalysed hydroformylation processes is the number of unwanted side reactions that result in the formation of undesirable side products, such as heavy ends and paraffins. These products not only impact negatively on the design of commercial processes but furthermore decrease the yield of the desirable and commercially valuable alcohol and/or aldehyde products from such a process.

Although phosphine-modified Co catalysed hydroformylation affords improved selectivity towards linear alcohols, another disadvantage is that reaction rates are generally far lower than those obtained with unmodified Co catalysis.

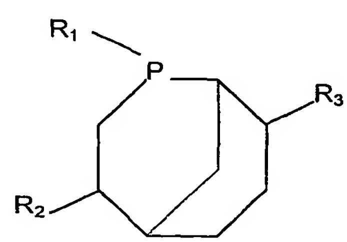
It is hence an object of this invention to provide a process for producing oxygenated products from an olefinic feedstock, whereby these problems are at least reduced.

Thus, according to a first aspect of the invention, there is provided a process for producing oxygenated products from an olefinic feedstock, which process includes reacting, in a hydroformylation reaction stage, an

olefin feedstock with carbon monoxide and hydrogen at elevated temperature and superatmospheric pressure in the presence of a hydroformylation catalyst comprising a mixture or combination of a metal, M, where M is cobalt (Co), rhodium (Rh), ruthenium (Ru) or palladium (Pd); carbon monoxide; and a bicyclic tertiary phosphine having a ligating phosphorus atom, with the ligating phosphorus atom being neither in a bridgehead position nor a member of a bridge linkage, to produce oxygenated products comprising aldehydes and/or alcohols.

The metal, M, may be any one of cobalt, rhodium, ruthenium or palladium; however, cobalt is preferred.

In particular, the bicyclic tertiary phosphine of the hydroformylation catalyst may be a [3.3.1]phosphabicyclononane represented by formula (III):

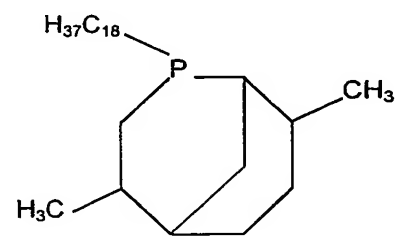


III

where R_1 is an alkyl, branched alkyl, cycloalkyl, or aryl group;
R_2 is an alkyl group; and
R_3 is an alkyl group.

More particularly, R_1 of the [3.3.1]phosphabicyclononane of formula (III) may be a linear C_2 to C_{20} hydrocarbon chain; and $R_2 = R_3$. Still more particularly, R_2 and R_3 may each be methyl.

The family of ligands of formula (III) in which $R_2 = R_3 =$ methyl is named Lim (as these ligands are limonene derived); thus, each ligand can be denoted 'Lim', together with a suffix corresponding to the carbon number of R_1. In one embodiment of the invention, the ligand may be Lim-18. Thus, Lim-18 will be represented by the formula **IV**, where R_1 is $C_{18}H_{37}$.



IV

In another embodiment of the invention, the ligand may be Lim-10. In other words, R_1 of the [3.3.1]phosphabicyclononane of formula (III) is then $C_{10}H_{21}$.

The reaction temperature may be from 100°C to 300°C, typically from 150°C to 200°C.

The reaction pressure may be at least 20 bar (150psi), preferably between 50 bar (750psi) and 100 bar (1500psi), typically about 85 bar (1232psi).

The hydroformylation reaction stage may be provided by a reactor capable of handling a homogenously catalysed chemical transformation, such as a continuous stirred tank reactor ('CSTR'), bubble column, or the like.

The olefinic feedstock may, in particular, be a C_2 to C_{20} Fischer-Tropsch derived olefin stream. Thus, the olefinic feedstock may be that obtained by subjecting a synthesis gas comprising carbon monoxide and hydrogen to Fischer-Tropsch reaction conditions in the presence of an iron-based, a cobalt-based or an iron/cobalt-based Fischer-Tropsch catalyst, with the resultant olefinic product then constituting the olefinic feedstock of the process of the invention, or a component thereof constituting the olefinic feedstock of the process of the invention.

In other words, the olefinic product from the Fischer-Tropsch reaction can, if necessary, be worked up to remove unwanted components therefrom and/or to separate a particular olefinic component therefrom, with said particular olefinic component then constituting the olefinic feedstock of the process of the invention.

According to a second aspect of the invention, there is provided a hydroformylation catalyst which includes, as a first component, a metal M, where M is cobalt, rhodium, ruthenium, or palladium; as a second component, carbon monoxide; and, as a third component, a bicyclic tertiary phosphine having a ligating phosphorus atom, with the ligating phosphorus atom being neither in a bridgehead position nor a member of a bridge linkage, to produce oxygenated products comprising aldehydes and/or alcohols, with the components being in the form of a mixture.

The metal M and the bicyclic tertiary phosphine may be as hereinbefore described with respect to the first aspect of the invention.

The invention will now be described by way of example, with reference to the following drawings.

In the drawings,

FIGURE 1 shows a simplified flow diagram of a process according to the invention for producing oxygenated products from an olefinic feedstock; and

FIGURE 2 shows, for Example 6, the formation of side products with time for Lim-18.

Referring to Figure 1, reference numeral 10 generally indicates a process according to the invention for producing oxygenated products from an olefinic feedstock.

The process 10 includes a hydroformylation stage 12, with an olefinic feedstock flow line 14 as well as a synthesis gas feed line 16 leading into the stage 12. A product withdrawal line 18 leads from the hydroformylation stage 12.

The process 10 includes a separation stage 20 into which the line 18 leads, with a product withdrawal line 22 leading from the stage 20. An unreacted feedstock recycle line 24, for recycling unreacted feedstock which is separated from the product produced, leads from the stage 20 back to the stage 12. A catalyst recycle line 26 also leads from the stage 20 back to the stage 12, for recycling catalyst which is separated from the product in the stage 20, back to the stage 12.

In use, a Fischer-Tropsch derived olefinic feedstock is fed into the stage 12 along the flow line 14, as is a synthesis gas comprising a mixture of carbon monoxide and hydrogen, which enters the stage 12 along the flow line 16. In the stage 12, the olefinic feedstock reacts with the carbon monoxide and hydrogen in the presence of a catalyst comprising an intimate mixture or combination of cobalt, carbon monoxide and a bicyclic tertiary phosphine having formula (IV), ie Lim-18, hereinbefore described. The temperature in the hydroformylation stage 12 is typically

around 170°C, while the pressure is typically around 85 bar (1232psi). Oxygenated products, consisting mainly of alcohols, are produced, and are withdrawn along the line 18 for further work-up.

The hydroformylation reaction stage 12 typically comprises a hydroformylation reactor system incorporating catalyst recovery and/or catalyst recycle.

EXAMPLES

In the Examples hereinafter given, all reactions were carried out in a 300 ml stainless steel stirred autoclave operated at 1200 rpm at the desired constant pressure with syngas delivered on demand. For each run the olefin, paraffinic solvent, and required amount of catalyst stock solution were loaded into the autoclave under argon, the reactor closed and purged with syngas, ie synthesis gas comprising a mixture of carbon monoxide and hydrogen, and then heated to the desired reaction temperature at atmospheric or ambient pressure. The reactions were initiated by pressurising with syngas to the desired reaction pressure. The syngas employed was a commercially available 2:1 mixture of hydrogen and carbon monoxide. Catalyst stock solutions were prepared using cobalt (2) octanoate and the appropriate ligand (EP, Lim-18 or Lim-10) in the required ratios. The olefins employed were 1-dodecene and a Fischer-Tropsch derived $C_{13/14}$ olefin feedstock.

EXAMPLE 1: Comparative example

Hydroformylation of 1-dodecene was carried out out in the manner described above. Using standard conditions of 85 bar of 2:1 H_2:CO syngas, 1000 ppm Co and a 2:1 ligand to metal molar ratio, hydroformylations were carried out at different temperatures to determine reaction rate and conversions. Rate constants were determined from analysis of gas uptake data, and conversions were based on GC analysis of samples taken at 2 hours. Results are summarised in Table 1.

TABLE 1: Comparative catalyst reactivity in hydroformylation of 1-dodecene

Ligand / Temperature (°C)	k' (h^{-1})	Conversion
Lim-18 / 170°C	0.82	99%
EP / 170°C	0.46	74%
Lim-18 / 180°C	1.54	99%
EP / 180°C	0.70	87%
Lim-18 / 190°C	2.69	100%
EP / 190°C	1.14	96%

EXAMPLE 2: Comparative example

Hydroformylation of 1-dodecene was carried out out in the manner described above. Using standard conditions of 170°C, 85 bar of 2:1 H_2:CO syngas and 1000 ppm Co, the ligand to metal ratio was changed. Paraffin formation was determined from GC analysis of the hydroformylation reaction mixture sampled after 2 hours. Results are summarised in Table 2.

TABLE 2: Paraffin formation in hydroformylation of 1-dodecene

Ligand / L:M	Paraffin (mass %)
Lim-18 / 2:1	5.39
EP / 2:1	8.50
Lim-18 / 4:1	6.98
EP / 4:1	10.99
Lim-18 / 8:1	8.12
EP / 8:1	11.43

As seen from Table 2, an undesirable side-reaction where a portion of the olefinic feedstock (1-dodecene) is converted to a saturated hydrocarbon (dodecane) is much less prominent when the LIM-18 catalyst system is employed in the hydroformylation process.

EXAMPLE 3: Comparative example

Exhaustive hydroformylation of 1-dodecene was carried out in the manner described above, with reaction conditions of 170°C, 85 bar of 2:1 H_2:CO syngas, 1000 ppm Co and 2:1 ligand to metal molar ratio. High temperature GC analysis of the reaction mixtures was carried out to quantify formation of heavy ends. As seen from Table 3, the formation of unwanted "heavies" fractions are suppressed when the LIM catalyst system is employed.

TABLE 3: Heavies formation in hydroformylation of 1-dodecene

LIGAND	HEAVIES (mass %)
EP	1.56%
Lim-18	1.36%

EXAMPLE 4:

Hydroformylation of a Fischer-Tropsch-derived $C_{13/14}$ olefin feed was carried out in the manner described above using Lim-18 as ligand, with reaction conditions of 170°C, 85 bar of 2:1 H_2:CO syngas, 1000 ppm Co and 2:1 ligand to metal molar ratio. As can be seen from Table 4, the calculated k' values for this reaction compare very well to those obained from pure feedstock.

TABLE 4: Comparison of feedstocks

Feedstock	k' (h^{-1})
$C_{13/14}$ Fischer-Tropsch-derived	0.81
1-dodecene	0.82

EXAMPLE 5:

Hydroformylation of 1-dodecene was carried out in the manner described above using Lim-10 as ligand, with reaction conditions of 170°C, 85 bar of 2:1 H_2:CO syngas, 1000 ppm Co and 2:1 ligand to metal molar ratio. As can be seen in Table 5, a ligand with a shorter alkyl chain affords comparable reactivity.

TABLE 5: Effect of ligand alkyl chain

Ligand	k' (h^{-1})
Lim-18	0.82
Lim-10	0.80

EXAMPLE 6:

A sampling run in a 600 ml autoclave was carried out for hydroformylation of 1-dodecene using Lim-18 as ligand. Reaction conditions of 170°C, 85 bar of 2:1 H_2:CO syngas, 1000 ppm Co and 2:1 ligand to metal molar ratio were employed, and samples were taken at various time intervals and analysed by GC to determine paraffin make with time. The results are indicated in Figure 2.

EXAMPLE 7:

Hydroformylation of 1-dodecene was carried out in the manner described above, with reaction conditions of 170°C, 85 bar of 2:1 H_2:CO syngas, 1000 ppm Co and 4:1 ligand to metal molar ratio. As can be seen in Table 6, ligands in accordance with the invention and where R_1 is not a linear alkyl chain (in this example, aryl or cycloalkyl) provide comparable reactivities.

TABLE 6: Effect of R_1

Ligand / R_1	k' (h^{-1})
III / phenyl	0.41
III / cyclopentyl	0.44
Lim-18	0.36

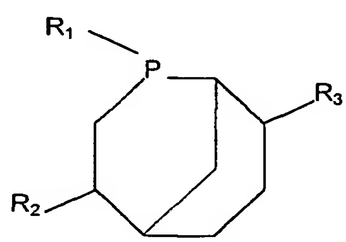
Thus, it has surprisingly been found that reaction rate is increased and the number of side reactions in the hydroformylation process is reduced if a novel catalyst consisting of a complex mixture of cobalt, carbon monoxide and a bicyclic tertiary phosphine where the ligating phosphorus atom is neither in a bridgehead position nor a member of a bridge linkage, is used as a hydroformylation catalyst, with either pure olefinic feedstocks or with olefinic feedstocks derived from Fischer-Tropsch processes. While the phosphorus atoms in ligands (I) and (II) are bridge linkages and thus shared between both heterocyclic rings, the ligating phosphorus atom in ligands (III) and (IV) forms part of only one ring in the bicyclic system. In contrast to ligands (I) and (II) where the phosphorus atom is flanked by two tertiary carbons, the ligating phosphorus atom is connected to a tertiary as well as to a secondary carbon atom in ligands (III)/(IV). It was thus surprisingly found that these structural differences resulted in an improved catalyst system so that these structural differences are thus apparently critical.

CLAIMS

1. A process for producing oxygenated products from an olefinic feedstock, which process includes reacting, in a hydroformylation reaction stage, an olefin feedstock with carbon monoxide and hydrogen at elevated temperature and superatmospheric pressure in the presence of a hydroformylation catalyst comprising a mixture or combination of a metal, M, where M is cobalt (Co), rhodium (Rh), ruthenium (Ru) or palladium (Pd); carbon monoxide; and a bicyclic tertiary phosphine having a ligating phosphorus atom, with the ligating phosphorus atom being neither in a bridgehead position nor a member of a bridge linkage, to produce oxygenated products comprising aldehydes and/or alcohols.

2. A process according to Claim 1, wherein, in the hydroformylation catalyst, M is cobalt.

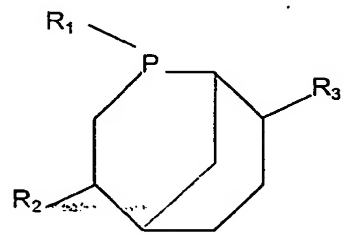
3. A process according to Claim 1 or Claim 2, wherein the bicyclic tertiary phosphine of the hydroformylation catalyst is a [3.3.1]phosphabicyclononane represented by formula (III):



III

where R_1 is an alkyl, branched alkyl, cycloalkyl, or aryl group;
R_2 is an alkyl group; and
R_3 is an alkyl group.

4. A process according to Claim 3, wherein the [3.3.1]phosphabicyclononane of the hydroformylation catalyst is:



III

where R_1 is an alkyl group;
R_2 is methyl; and
R_3 is methyl.

5. A process according to Claim 3 or Claim 4, wherein, in the hydroformylation catalyst, R_1 of the [3.3.1]phosphabicyclononane of formula (III) is a linear C_2 to C_{20} hydrocarbon chain.

6. A process according to Claim 5, wherein, in the hydroformylation catalyst, R_1 of the [3.3.1]phosphabicyclononane of formula (III) is $C_{18}H_{37}$.

7. A process according to Claim 5, wherein, in the hydroformylation catalyst, R_1 of the [3.3.1]phosphabicyclononane of formula (III) is $C_{10}H_{21}$.

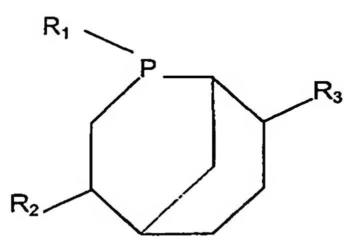
8. A process according to any one of Claims 1 to 7 inclusive, wherein the reaction temperature is from 100°C to 300°C, while the reaction pressure is at least 20 bar.

9. A process according to any one of Claims 1 to 8 inclusive, wherein the olefinic feedstock is a C_2 to C_{20} Fischer-Tropsch derived olefinic stream.

10. A hydroformylation catalyst which includes, as a first component, a metal M, where M is cobalt, rhodium, ruthenium, or palladium; as a second component, carbon monoxide; and, as a third component, a bicyclic tertiary phosphine having a ligating phosphorus atom, with the ligating phosphorus atom being neither in a bridgehead position nor a member of a bridge linkage, to produce oxygenated products comprising aldehydes and/or alcohols, with the components being in the form of a mixture.

11. A hydroformylation catalyst according to Claim 10, wherein M is cobalt.

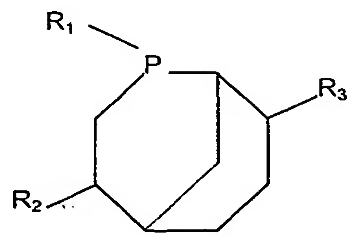
12. A hydroformylation catalyst according to Claim 10 or Claim 11, wherein the bicyclic tertiary phosphine is a [3.3.1]phosphabicyclononane represented by formula (III):



III

where R_1 is an alkyl, branched alkyl, cycloalkyl or aryl group;
R_2 is an alkyl group; and
R_3 is an alkyl group.

13. A hydroformylation catalyst according to Claim 12, wherein the [3.3.1]phosphabicyclononane is:



III

where R_1 is an alkyl group;
R_2 is methyl; and
R_3 is methyl.

14. A hydroformylation catalyst according to Claim 12 or Claim 13, wherein R_1 of the [3.3.1]phosphabicyclononane of formula (III) is a linear C_2 to C_{20} hydrocarbon chain.

15. A hydroformylation catalyst according to Claim 14, wherein R_1 of the [3.3.1]phosphabicyclononane of formula (III) is $C_{18}H_{37}$.

16. A hydroformylation catalyst according to Claim 14, wherein R_1 of the [3.3.1]phosphabicyclononane of formula (III) is $C_{10}H_{21}$.

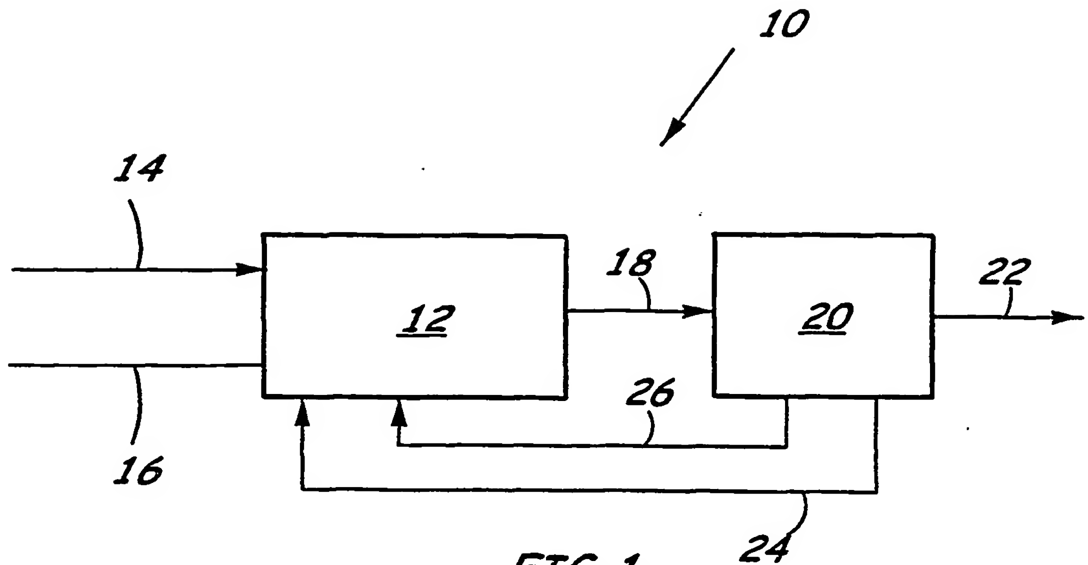


FIG 1

EP vs Lim - 18 (Dodecane Formation)

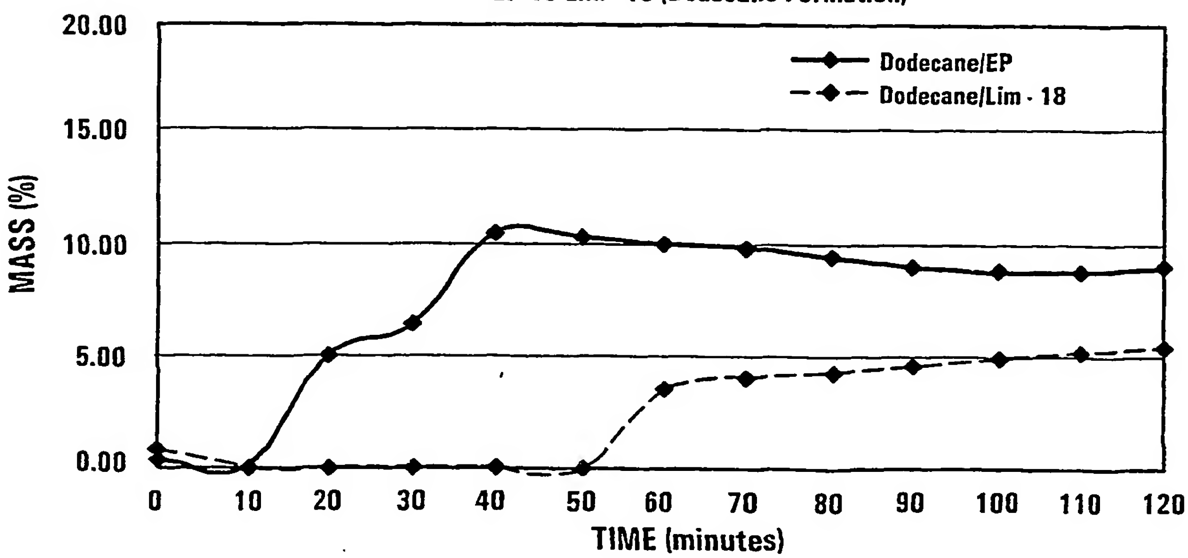


FIG 2

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(54) Title: BICYCLIC PHOSPHIN COMPRISING HYDROFORMYLATION CATALYST AND USE THEREOF IN PRODUCTION OF OXYGENATED PRODUCTS

(57) Abstract: A process for producing oxygenated products from an olefinic feedstock, which process includes reacting, in a hydroformylation reaction stage, an olefin feedstock with carbon monoxide and hydrogen at elevated temperature and superatmospheric pressure in the presence of a hydroformylation catalyst. The hydroformylation catalyst comprises a mixture of a metal, M, where M is cobalt (Co), rhodium (Rh), ruthenium (Ru) or palladium (Pd); carbon monoxide; and a bicyclic tertiary phosphine having a ligating phosphorus atom. The ligating phosphorus atom is neither in a bridgehead position nor a member of a bridge linkage. The process produces oxygenated products comprising aldehydes and/or alcohols.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J31/24 C07C45/50 C07C29/16 C07C31/125 C07F9/6568
C07F15/00 C07F15/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98 45040 A (DSM N.V.) 15 October 1998 (1998-10-15) example IV ---	1-16
Y	GB 1 109 787 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V.) 18 April 1968 (1968-04-18) the whole document ---	1-16
Y	GB 1 254 063 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V.) 17 November 1971 (1971-11-17) the whole document ---	1-16
P,Y	WO 01 16260 A (IMPERIAL CHEMICAL INDUSTRIES PLC) 8 March 2001 (2001-03-08) example 4 -----	1-16

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 March 2002	02/04/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Beslier, L

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IB 01/01452

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